Introduction

Supercritical (SC) water is an interesting medium for many chemical reactions and may become very useful for the removal of hazardous waste [1]. A detailed description of chemical reactions in SC conditions requires knowledge of ion hydration. The partial radial distribution function (RDF) around each solute atom can be determined by x-ray absorption fine structure (XAFS). However, XAFS misses the broad features of the partial RDF that correspond to the low-\(q\) portion of the structure factor (\(q<6\text{Å}^{-1}\)) and thus in liquids it is difficult to obtain structural information beyond the first coordination shell. Differential anomalous x-ray scattering (DAS) [2] in aqueous solutions is based on measuring diffuse x-ray scattering at several different photon energies near an absorption edge of one of the solute species in the sample. The difference between the structure factors obtained at two energies is the partial structure factor related to the partial RDF around the anomalous scatterer. DAS provides the low- and mid-range components of the RDF in \(q\)-space and thus supplements the structural information obtained from XAFS. We are developing a system to measure DAS from SC aqueous solutions.

Methods and Materials

The x-ray scattering measurements are done in transmission geometry using a Rowland circle monochromator of radius 10 inches to reject inelastic scattered photons (Compton and resonant Raman scattering). The sample cell is positioned at the focal point of the Rowland circle (Figure 1). The whole Rowland circle apparatus is placed on a large rotary table with the sample center at the rotation axis of the table so that the elastic scattering intensity can be measured as a function of scattering angle by rotating the table. The monochromator uses a bent Si crystal whose bending and distance from the center of the Rowland circle can be tuned to maximize the intensity reflected by the crystal. The crystal bender was designed to allow easy swapping of crystals so that the monochromator can operate over a large energy range. The reflected x-rays are focused to a detector, which is placed behind a slit on the other focal point of the circle.

The high temperature and pressure sample cell is made of a small boron carbide (BC) hollow cylinder, which is pressed between two titanium tubes. These are held together by a titanium alloy block, which holds also the heating elements. The block is thermally insulated inside a vacuum chamber. The titanium tubes are connected to a pump that maintains high pressure and can be used to flow the solution through the cell. The BC tube can hold substantial pressures and is quite resistant to the SC corrosive conditions and has a relatively low x-ray absorption. The polycrystalline BC adds diffraction peaks to the diffuse scattering signal, but the spatial resolution of the Rowland circle monochromator enables to reject these peaks at scattering angles larger than about 30°. The few diffraction peaks at smaller scattering angles can be eliminated from the scattering data without damaging its quality. The intensity of the beam transmitted through the cell is measured by another detector to monitor any changes in the solution density due to formation of precipitates or bubbles in the solution.

Results

The energy resolution of the monochromator was found to be 28 eV at a photon energy of 12000 eV using a <400> Si crystal. This is sufficient to reject completely resonant Raman scattering and to reject Compton scattering above a scattering angle of about 30°. Preliminary diffuse scattering measurements from aqueous solutions have yielded data reproducible enough to permit DAS measurements during our next run.
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References